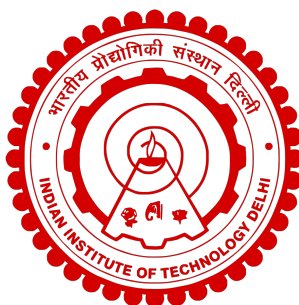


METAL NANOCLOUDS: ATOMISTIC INSIGHTS FROM COMPUTATIONAL MODELING

VIKAS TIWARI



**DEPARTMENT OF CHEMISTRY
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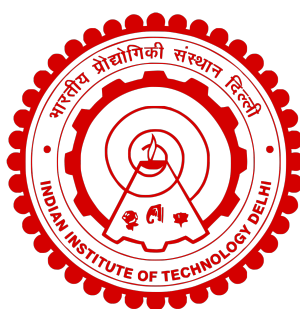
by

Vikas Tiwari

DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirement of the degree of doctor of philosophy to the



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May 2026

Dedicated to
my mother, Sheela

CERTIFICATE

This is to certify that the thesis entitled “*Metal Nanoclusters: Atomistic Insights from Computational Modeling*” being submitted by **Mr. Vikas Tiwari** to the **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him under my supervision and guidance.

Mr. Vikas Tiwari has fulfilled all the requirements for the submission of his Ph.D. thesis, and to the best of my knowledge, the work embodied in this thesis has attained the requisite standard and is worthy of consideration for the award of the Ph.D. degree.

The contents of this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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Vikas Tiwari

New Delhi, 06 May 2026



AIMDES group photo taken on August, 2025. From left to right: *Sonam, Nistha, Neha, Shilpi, Nisha, Rishu, Prof. Tarak, Me, Soumya, Anmol, Dhananjay, Sachin, and Animesh.*



Abstract

Atomically precise monolayer-protected metal nanoclusters (MPCs) have emerged as an important class of materials bridging the gap between molecular and metallic regimes. Understanding MPCs' behavior at the atomistic level is crucial, as their formation, stability, and functionality in catalysis are all governed by their atomic-scale structure and dynamics. However, direct experimental observation of the structural and dynamic evolution of MPCs in the condensed phase remains challenging and costly due to the inherent limitations of current techniques in reaching the nanoscale size and time resolution. Computer simulations, in particular, molecular dynamics (MD) simulations, provide the scope for studying a system and relevant processes at this resolution and unveil microscopic and dynamic details. In this thesis, advanced computational approaches, combining state-of-the-art MD simulations, enhanced sampling (ES) methods, hybrid quantum mechanics/molecular mechanics (QM/MM) schemes, and machine-learned interatomic potentials (MLIP) based simulation are employed to model MPCs and unravel their formation, self-assembly, interactions with biomolecules, and catalytic activity.

First, we leveraged MLIP-based ES simulations to elucidate the fundamental mechanism of nanocluster formation from solution. These simulations capture the stepwise nucleation of MCPs *via* aggregation of staple motifs followed by dynamic rearrangement, providing atomic-level insights into the thermodynamic and kinetic factors governing nanocluster formation ([chapter 3](#)).

Next, we investigated the spontaneous self-assembly of MPCs to macromolecular aggregates. Our simulations reveal inter-ligand hydrogen bonding, steric effects, and counter ion coordination act cooperatively to direct cluster aggregation and the emergence of ordered superstructures, highlighting the key intermolecular forces driving supramolecular self-assembly ([chapter 4](#)). We then explored peptide-MPC interactions through classical MD and ES simulations, uncovering how MPC ligands

interact with specific amino acids of the peptide, thereby stabilizing it on the MPC surface ([chapter 5](#)). In [chapter 6](#) we used QM/MM MD simulations to investigate how MPC catalyses chemical reaction.

Finally, extending our investigation to heterogeneous environments, we modeled the dynamics of a bare nanocluster (Au_8) adsorbed on F-center defect sites of MgO surfaces. MLIP-based ES simulations capture dynamics of Au_8 near the F-center defect, binding of CO on Au_8 , and its oxidation mechanism in the presence of O_2 ([chapter 7](#)).

Overall, the works presented in this thesis provide an integrated multiscale computational framework to study important physico-chemical processes, starting from MPCs formation to their potential application in catalysis and as a drug carrier. The outcomes of this thesis paves the way for rational design and development of next generation metal nanoclusters.

Keywords: Atomically-precise metal nanoclusters | Molecular dynamics simulation | Nucleation | Self-assembly | Catalysis | Enhanced Sampling | Machine-learned inter-atomic potentials | QM/MM

सार

परमाणु-स्तर पर सटीक मोनोलायर-संरक्षित धातु नैनोक्लस्टर (MPCs) ऐसे महत्वपूर्ण पदार्थों के रूप में उभरे हैं जो आणविक और धात्विक अवस्थाओं के बीच की कड़ी का कार्य करते हैं। MPCs के व्यवहार को परमाणु स्तर पर समझना अत्यंत आवश्यक है, क्योंकि उनका निर्माण, स्थिरता तथा उत्प्रेरण (catalysis) में उनकी कार्यक्षमता उनके परमाणु-स्तरीय संरचना और गतिशीलता द्वारा नियंत्रित होती है। किन्तु, वर्तमान प्रायोगिक तकनीकों की सीमाओं के कारण संघनित अवस्था में MPCs की संरचनात्मक तथा गतिशील उत्क्रांति का प्रत्यक्ष अवलोकन करना कठिन और महंगा है, विशेषकर नैनोस्तरीय आकार और समय-मान पर। कंप्यूटर सिमुलेशन, विशेष रूप से आणविक गतिकी (Molecular Dynamics; MD) सिमुलेशन, इन प्रणालियों तथा उनसे संबंधित प्रक्रियाओं का अध्ययन इस स्तर पर करने और सूक्ष्म संरचनात्मक एवं गतिशील विवरण प्राप्त करने की क्षमता प्रदान करते हैं। इस शोधप्रबंध में उन्नत संगणनात्मक विधियों—जिनमें अत्याधुनिक MD सिमुलेशन, एन्हांस्ड सैंपलिंग (Enhanced Sampling; ES) तकनीकें, हाइब्रिड क्वांटम मैकेनिक्स/मॉलिक्यूलर मैकेनिक्स (QM/MM) योजनाएँ, तथा मशीन-लर्नड इंटरएटोमिक पोटेंशियल (MLIP) आधारित सिमुलेशन शामिल हैं—का उपयोग MPCs का मॉडल तैयार करने तथा उनके निर्माण, स्व-संयोजन (self-assembly), जैव-अणुओं के साथ अंतःक्रिया और उत्प्रेरक गतिविधि को समझने के लिए किया गया है। सबसे पहले, हमने MLIP-आधारित ES सिमुलेशन का उपयोग कर विलयन से नैनोक्लस्टर निर्माण की मूलभूत प्रक्रिया को स्पष्ट किया। इन सिमुलेशनों ने स्टेपल मोटिफ़ के क्रमिक एकत्रीकरण तथा उसके बाद होने वाले गतिशील पुनर्विन्यास के माध्यम से MPCs के नाभिकीयन (nucleation) को दर्शाया, जिससे नैनोक्लस्टर निर्माण को नियंत्रित करने वाले ऊष्मागतिकीय और गतिज कारकों के बारे में परमाणु-स्तरीय जानकारी प्राप्त हुई (chapter 3)। इसके पश्चात्, हमने MPCs के स्वतः स्व-संयोजन द्वारा बड़े अणुगत समुच्चयों (macromolecular aggregates) के निर्माण का अध्ययन किया। हमारे सिमुलेशन दर्शाते हैं कि लिगेण्डों के बीच हाइड्रोजन बंधन, स्थैतिक अवरोध (steric effects), तथा काउंटर-आयन समन्वय मिलकर क्लस्टरों के एकत्रीकरण और सुव्यवस्थित सुपर-संरचनाओं के निर्माण को निर्देशित करते हैं। इससे स्व-संयोजन को प्रेरित करने वाले प्रमुख अंतर-अणुगत बलों की पहचान हुई (chapter 4)। इसके बाद, हमने क्लासिकल MD तथा ES सिमुलेशन की सहायता से पेप्टाइड-MPC अंतःक्रियाओं का अध्ययन किया, जिससे यह स्पष्ट हुआ कि MPC के लिगेण्ड पेप्टाइड के विशिष्ट अमीनो अम्लों के साथ किस प्रकार अंतःक्रिया करते हैं और उसे MPC सतह पर स्थिर बनाते हैं (chapter 5)। chapter 6 में हमने

QM/MM MD सिमुलेशन का उपयोग कर यह अध्ययन किया कि MPC किस प्रकार रासायनिक अभिक्रियाओं का उत्प्रेरण करता है। अंततः, विषम (heterogeneous) परिवेशों में अपने अध्ययन का विस्तार करते हुए, हमने MgO सतहों पर F-center दोष स्थलों पर अधिशोषित नग्न नैनोक्लस्टर (Au_8) की गतिशीलता का मॉडल तैयार किया। MLIP-आधारित ES सिमुलेशन ने F-center दोष के समीप Au_8 की गतिशीलता, Au_8 पर CO के बंधन तथा O_2 की उपस्थिति में उसके ऑक्सीकरण तंत्र को सफलतापूर्वक प्रदर्शित किया (chapter 7)। समग्र रूप से, इस शोधप्रबंध में प्रस्तुत कार्य MPCs के निर्माण से लेकर उत्प्रेरण तथा औषधि वाहक (drug carrier) के रूप में उनके संभावित अनुप्रयोगों तक महत्वपूर्ण भौतिक-रासायनिक प्रक्रियाओं के अध्ययन हेतु एक समेकित बहु-स्तरीय (multiscale) संगणनात्मक ढाँचा प्रदान करते हैं। इस शोध के निष्कर्ष अगली पीढ़ी के धातु नैनोक्लस्टरों के तर्कसंगत डिज़ाइन और विकास का मार्ग प्रशस्त करते हैं।

कुंजी शब्द: परमाणु-सटीक धातु नैनोक्लस्टर | आणविक गतिकी सिमुलेशन | नाभिकीयन | स्व-संयोजन | उत्प्रेरण | एन्हांस्ड सैंपलिंग | मशीन-लर्न इंटरएटोमिक पोटेंशियल | QM/MM

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